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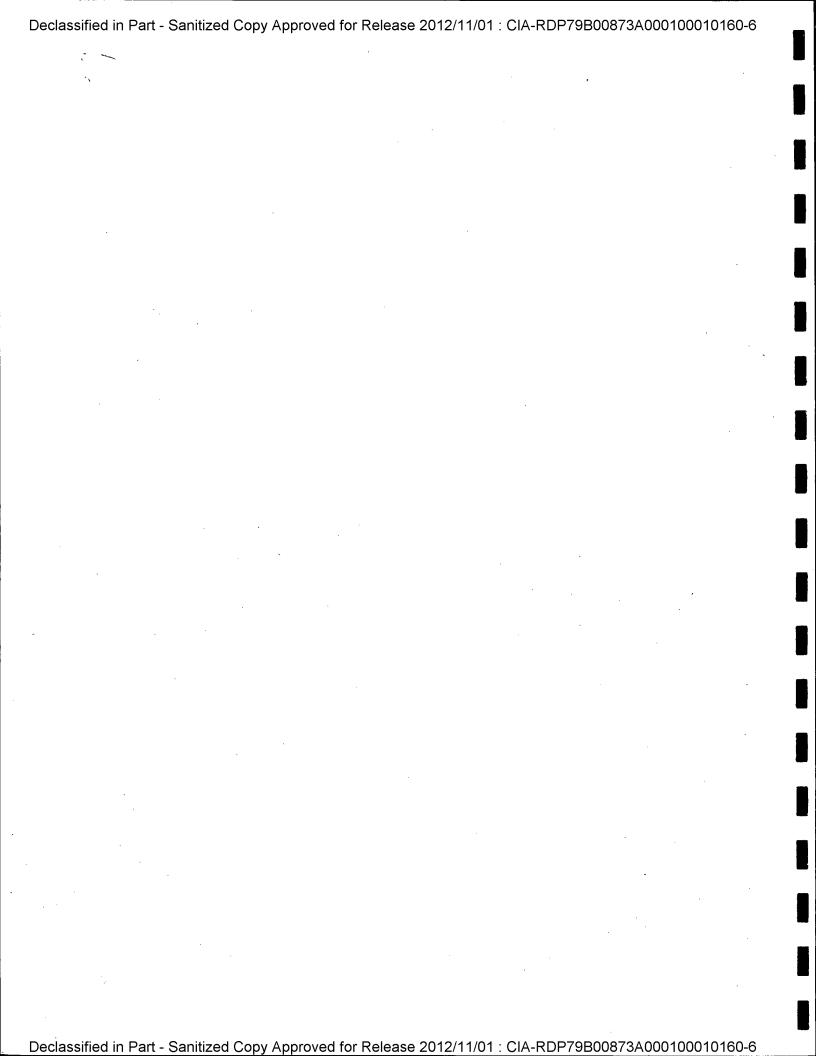
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#### PURPOSE

The purpose of this short program was to test the hypothesis that the nature of the developed silver in a processed photographic negative changes in the region of a developed edge; that this change might be measured by spectral microdensitometry; that the measurements might be used as a diagnostic tool in evaluating the quality of processing; and that the measurements might ultimately give an indication of the image quality. Specifically, we were to perform a microdensitometer study of developed edges using two spectrally different light probes in the microdensitometer of 400 nm (= 4000 Å) and 700 nm. Basing our studies on two well-known photographic effects,

- 1. the adjacency effect, and
- 2. the variation in the spectral color of developed silver with developer and development conditions,

we were to determine if there is a variation in the color of the developed silver along the microdensitometer trace of the edge. If such a color change along the edge is observed, we were to determine if the difference between the spectral microdensitometer traces could be correlated with the uniformity or quality of the processing.

#### CONCLUSIONS

Experiments were performed on Kodak Plus-X Pan film using three developers, in all cases at 68°F and with controlled agitation:

1. Kodak D-19, 5 min — a conventional strong superadditive developer

2. XDR-4, 10 min — a soft-working, superadditive developer

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3. BN-1A, 10 min — a very soft non-superadditive solvent developer.

The high density region of the developed edge is called  $D_{max}$ , and the low density background of the edge is called  $D_{min}$ . Exposures were adjusted so that  $D_{max}$  was

about 0.8. The  $D_{\min}$  fog level was about 0.3 because of the blue film base. Microdensitometer traces of the developed edge images from  $D_{\min}$  to  $D_{\max}$  were made in blue light of 400 nm, and in red light of 700 nm. The curves were normalized at  $D_{\min}$  to correct for film base color. Following conventional nomenclature, we refer to the densities so read as D(400) and D(700), and the normalized ratio D(400)/D(700) is called the "color ratio."

Our conclusions are as follows:

- 1. For images developed in D-19, the edge traces of Figure 1 were produced. There is no significant adjacency effect. The slight increase of the color ratio D(400)/D(700) at  $D_{max}$ , compared to  $D_{min}$ , is in conformance with results in the literature. The differential curve D(400)-D(700) shows no inflection or reversal near the edge; hence the color change is not associated with the structure of the edge.
- 2. For images developed in T/O XDR-4, the edge traces of Figure 2 were produced. A border or Mackie line adjacency edge in the high density region is

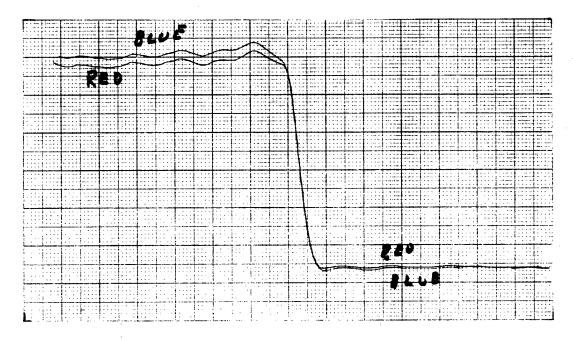


Figure 1. Microdensitometer Traces of Edge Images Made in Blue Light (400 nm) and Red Light (700 nm) Developed in D-19 for 5 min

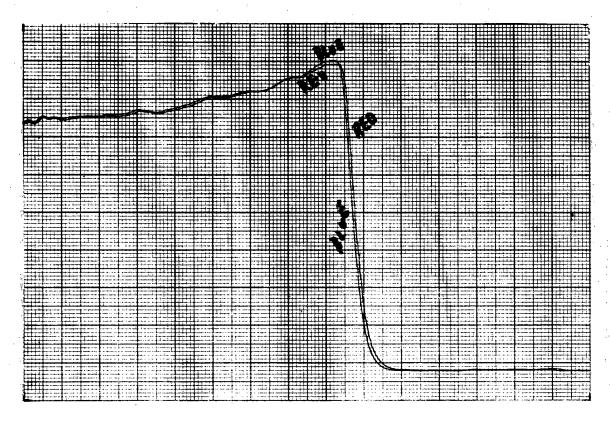


Figure 2. Microdensitometer Traces of Edge Images Made in Blue Light (400 nm) and Red Light (700 nm) Developed in XDR-4 for 10 min

apparent. The color ratio D(400)/D(700) in the region of the edge is virtually unity for this developer, and the differential between the two traces is virtually zero (there is a shift of about  $2\mu$  between the two superposed traces); hence there is no color change associated with the structure of the edge.

- 3. For images developed in T/O BN-1A, the edge traces of Figure 3 were produced. They show a significant adjacency border edge effect. The color ratio D(400)/D(700) is high in the  $D_{max}$  region. However, the differential D(400)-D(700) shows no unusual behavior near the edge, and we do not associate the rise in color ratio with the edge or its adjacency peak.
- 4. On the basis of these results, there is an increase in color ratio of silver at  $D_{max}$  (in D-19 and in BN-1A), a fact consistent with the literature on the color of developed silver. However, there is no notable differential effect of D(400)-D(700)

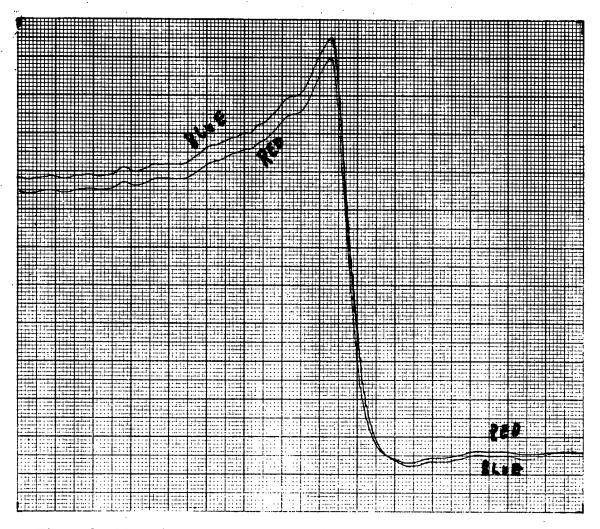


Figure 3. Microdensitometer Traces of Edge Images Made in Blue Light (400 nm) and Red Light (700 nm) Developed in BN-1A for 10 min

associated with the structure or adjacency behavior of the edge. On this basis, a diagnostic test of developer uniformity does not appear to have evolved from our work.

5. In pursuing this work, we note that sharp adjacency edges can be produced by use of the softer developers T/O XDR-4 and T/O BN-1A, compared with the use of the strong developer Kodak D-19. This adjacency spike might be used as a fiducial point for more accurate measurements using either D(400) or D(700) traces. Further work in this area might be justified.

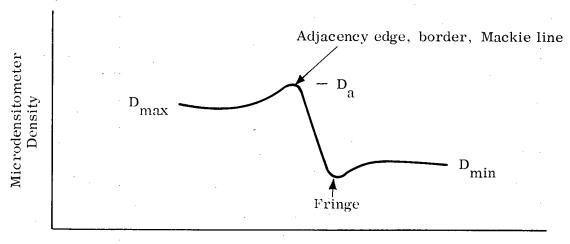
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#### BACKGROUND

Let us review the adjacency effect and spectral color of developed silver effect as they guided this program.

### ADJACENCY EFFECT

A microdensitometer trace of a photographically developed edge often resembles the structure shown in the sketch of Figure 4. Terminology for this effect has been summarized in the book by Mees. <sup>1</sup> The increase in density to D<sub>a</sub> at the edge of the dense area is often called the border, spike, or adjacency edge. Frequently, the dense line associated with the border is called the Mackie line; the decrease in density at the edge of the light area, the fringe; and the overall effect, the Eberhard effect. No recent publication has satisfactorily described this situation, but it is similar to Leisegang ring formation found in capillary tubes in nature, which has been explained by diffusion equations. A typical qualitative explanation for the Eberhard effect is as follows. The flux of developer flowing into any given area of the film is constant under uniform immersion and concentration conditions. Developer oxidation products are desensitizers, and they flow out abundantly in the region of heavy exposure. In the region of the border or spike, extra, fresh developer flows in from the adjacent underexposed region, since this developer is not being used to develop silver in the underexposed area. This locally increases the developer flux



Distance
Figure 4. Diagram of the Edge or Eberhard Effect

to the border region. The extra developer accounts for the border density or Mackie line. The region of the Mackie line discharges oxidation products preferentially into the clear region of the fringe line by osmotic equilibrium. The increased flux of oxidation products depresses development and accounts for the fringe line. This explanation involves the rates of development; accordingly, if the developer is very active (such as D-19) and if agitation is very effective (as in a spray operation), the adjacency effects are overcome. Weak-acting developers, which have lower development rates than stronger developers, will be more prone to adjacency behavior.

#### SPECTRAL COLOR OF DEVELOPER SILVER

Two recent papers  $^{2,3}$  consider the color of developed silver. In these papers, and in earlier work, the density of silver measured in blue light of 400 nm (= 4000 Å) is called D(400), and that measured in red light of 700 nm is called D(700). The ratio of these densities, D(400)/D(700), is called the "color ratio." In general, normal developers produce filamentary silver that has a color ratio greater than 1, indicating that the silver is reddish or warm. As the component of silver deposited from solution by physical development increases, the silver becomes more compact, the color becomes colder or bluish, and the color ratio decreases. The specific value of the color ratio depends on the film type and the developer.

#### PROGRAM RELATED TO ADJACENCY AND COLOR

It is clear that in the region of a photographic edge, there will be some tendency toward an adjacency effect. Since the adjacency effect depends on unequal local concentrations of developer, this could lead to a change in the color of the developed silver with edge structure. It is proper to ask if a change of color ratio occurs at the edge in the region of the adjacency border or fringe spikes. Such an effect should be measurable by spectral microdensitometer traces across the edge. If a color ratio change occurs, it could then be related to the uniformity of development, and perhaps ultimately to image quality. In fact, as we have noted in the conclusions and as we will show below, a change in color ratio does occur from the low to high density regions of the edge, but a change across the edge associated with edge structure does not occur.

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#### **EXPERIMENTAL**

#### MICRODENSITOMETER

All the traces on this program were made on the Joyce Loebl microdensitometer. A schematic diagram of this instrument is shown in Figure 5. It is a double beam balancing instrument in which the detector determines a null point. As shown in Figure 5, two beams are taken from the light source, the sample beam and the balancing beam. The sample beam goes through a pre-slit and a condenser, which images the pre-slit on the sample. The image of the sample, illuminated by the image of the pre-slit, is gathered up and magnified by the microscope objective, and is then directed onto the scanning slit. The sample beam, having passed through the scanning slit, is directed through a sample filter, then transmitted through the balance beam mirror, through the chopper, and onto the photomultiplier tube. The scanning slit is fixed in space and time, but the sample is on a driven stage. Therefore the image is driven across the scanning slit so that the slit effectively scans the image.

The balancing beam, which comes from the same light source as the sample beam, is directed first through a balancing filter and then through the calibrated variable balancing wedge. The balancing beam is then directed by the balance beam mirror through the chopper onto the photomultiplier tube. The photomultiplier acts as a null-detector, moving the balancing wedge by a servo mechanism until it modulates the balancing beam to equal that of the sample beam, that is, until the alternating sample and reference beams striking it are of equal intensity (null). The balancing wedge is directly coupled to the pen, so that the trace is a measure of the position of the balancing wedge. Since the wedge is calibrated in density units per centimeter of displacement, the resulting trace is directly in density units. For the traces of Figures 1 through 3 we used balancing wedge D-355, which covered a range of 0.071 density units per centimeter displacement.

We have noted that the sample, illuminated by the pre-slit, is magnified by a micro-scope objective. The optical system doubles the magnification of the objective. Throughout this study we used a 20X objective and so magnified the image of the edge 40X. The scanning slit on this instrument is fixed in space and time, and the magnified

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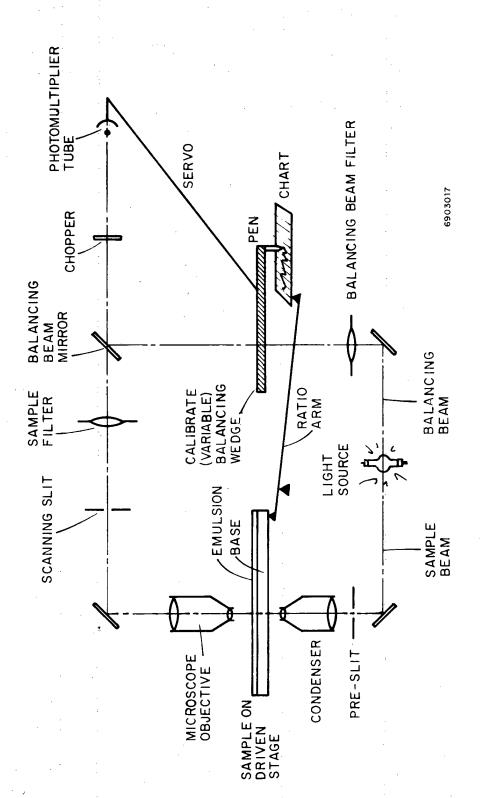


Figure 5. Schematic of Microdensitometer

image is driven across by the driven sample stage. The scanning slit is mechanically set. In each case we used two slit widths, 0.10 mm and 0.40 mm, with a slit length of 7 mm. The equivalent scanning slit widths on the film plane, to be quoted hereafter are 1/40X of these values, or  $2.5\,\mu$  and  $10\,\mu$  respectively. In Figures 1 through 3 a  $10\,\mu$  slit width was used. The equivalent slit height on the film plane is 7/40 = 0.175 mm.

To spread the linear dimension of the scan across the edge, a ratio arm is used to link the driven stage with the driven chart. For example, a ratio arm of 100:1 presents  $10\mu$  of driven length on the sample as  $100\times10\mu=1\,\mathrm{mm}$  of horizontal distance on the chart paper. In the edge traces of Figures 1 through 3 the ratio arm 500:1 was used, so that each millimeter of chart paper is equal to  $2\mu$  of sample on the film plane.

For standard traces in white light, no sample or balancing beam filters are used, and the photomultiplier supplied with the instrument, a 1P21 with S-4 response, is satisfactory. The response of the 1P21 at 700 nm is virtually zero; in fact, the preslit image is outlined with a disk of red light to allow visual alignment and focusing without causing response of the tube. A tube change and the use of filters were needed for our experiment.

To obtain response to red light of 700 nm, we replace the standard tube with a HTV-R136, Hamamatsu Ltd. The published response of this tube is S-10, as shown in Figure 6. To obtain traces in light of 400 nm, we introduced two blue filters, each an Ilford-304 (their spectral transmission is shown in Figure 6) in both the sample and balancing filter positions. Thus the photomultiplier saw light of the same spectral transmission in both sample and balancing beams. For traces in light of 700 nm, we also used two Ilford-204 filters in both sample and balancing beams. The spectral transmittance of this filter is also shown in Figure 6.

In this experiment we are looking for changes in spectral transmission of the image silver in the sample. Therefore we must be sure to correct for spectral effects that may appear in one beam of the instrument and not in the other. The balancing wedge in the balancing beam continuously varies in density over its length, and the attenuating medium is colloidal carbon. Therefore, we expect that the color ratio of this wedge

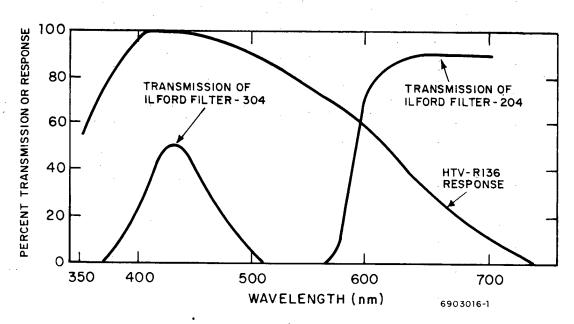


Figure 6. Tube Response Curve and Spectral Transmission of Filters

will vary slightly along its length. This could account for some separation of D(400) and D(700) with density. But it could not account for the strong difference in color separation we observe for two samples that have about the same  $D_{max}$ , for example the samples of Figures 1 and 2. These effects are striking, and the difference between them could not be explained by a constant change of color ratio of the balancing wedge.

The red illumination surrounding the jaws of the pre-slit in the sample beam would cause a response if seen by the HVT-R132 photomultiplier. However, the area of the pre-slit always overlaps the area of the scanning slit, so that the scanning slit should never see any red light. If some red light is scattered into the sample beam, it would augment the red transmission and decrease D(700). But as with the balancing beam effect, it could not account for the strongly different variation of color ratios in Figures 1 and 2 that occur at almost the same D<sub>max</sub>, and therefore at almost the same degree of illumination from the sample beam.

The film base of Plus-X is bluish for antihalation purposes. This blue base introduces into the sample beam a spectral component that is not present in the balancing beam. To cancel this out, in a comparison of D(400) and D(700) curves, we normalize the two curves at  $D_{\min}$ , so that a change in color at densities above  $D_{\min}$  results from silver color only.

#### EXPOSURE, DEVELOPMENT, TRACING

To obtain a reproducible image with sharp edges, we constructed a slit of nominal width, 2 mm, made by two stainless-steel razor blades assembled with black masking tape on a glass plate. This object was exposed to the photographic film on a contact printer using a blue G.E. A-1 Argon lamp at 30 inches for exposure, modulated with a filter of neutral density 1. Exposures of 1 through 16 seconds were made. To have comparable results with all three developers, and to use a single balancing wedge in the microdensitometer, we selected images for tracing that had about the same  $D_{max}$ ,  $D_{min}$ , and  $\Delta D$  values. For the film strips developed in XDR-4 and BN-1A, these were the 8-second exposures; for the film developed in D-19, it was the 2 second exposure. The  $D_{min}$  values were all about 0.3 (set by the blue film base), the  $D_{max}$  values were all about 0.8, and the  $\Delta D$  values were all about 0.5.

The film chosen for this study was Kodak Plus-X, 35 mm format, because edge enhancement effects were known to occur when images on this film are developed in XDR-4 developer.

Development was done by placing the film strips on processing racks, immersing the racks in deep tanks, and providing minor reproducible agitation of the racks in the tanks at 1-minute intervals. Processing was done at  $68^{\circ}$ F, 10 minutes for XDR-4 and BN-1A, and 5 minutes for D-19.

The formulations of the three developers used on this program are shown in Table 1. Kodak D-19 is a standard strong superadditive developer with some solvation because of the high concentration of sulfite. Various studies on low gamma and low granularity developers have been performed and published by Tech/Ops. 4,5,6 These developers generally give images with enhanced edge effects because of their low activity and relatively high solvation. Developer XDR-4 is milder in alkalinity than D-19, but stronger in solvation because of its ratio of sulfite to developer. Developer BN-1A, formulated for this program, is very mild since it is not superadditive, and has increased solvation as a result of the presence of thiocyanate (KSCN).

Table 1. Developers Used on This Program (all grams/liter of water)

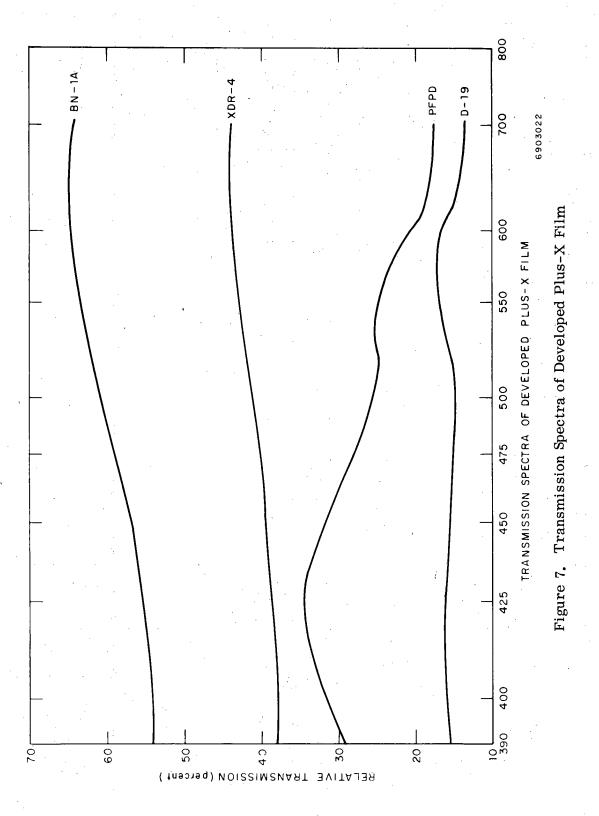
Content	Kodak D-19	XDR-4	BN-1A	
Metol	2.0	1	0.5	
Hydroquinone	8.0	1		
$K_2SO_3$		25	5	
$Na_2SO_3$	90.0			
$Na_2CO_3$	52.5		5	
NaHCO <sub>3</sub>		10		
KSCN			1	
KBr	5.0			
Comment	Strong	Mild	Weaker with Solvent	

#### RESULTS

#### SPECTRA OF DEVELOPED SILVER

We have noted that the spectral transmission of developed silver has been the subject of some study.  $^{1,2,3}$  The ratio of density of silver measured at 400 nm to that measured at 700 nm, D(400)/D(700), is known as the color ratio, and tends to be greater than 1. This means that the transmission of red light generally exceeds that of blue light, and the silver is reddish or warm.

The transmission spectra of silver developed on Plus-X film, using the three developers of Table 1 and also post-fixation silver physical development (PFPD), are shown in Figure 7. These curves were prepared by prefogging the film strips so that their developed density would be approximately 1. In Figure 7, these curves are superposed, but they are shifted with respect to their mean transmission so that all the traces could be included on one diagram. The  $\Delta T$  scale is constant for each curve, however. The color ratio (which is in density) will vary inversely as the transmission



ratios of Figure 7. Referring to Figure 6, let us consider the spectral and the color ratio D(400)/D(700):

- 1. D-19 shows a color ratio of about unity (neutral).
- 2. XDR-4 shows a color ratio greater than 1 (warm).
- 3. BN-1A shows a higher color ratio than that of XDR-4 (reddish).
- 4. Pure silver PFPD shows a color ratio less than unity (bluish or cold).

The curves of Figure 7 show us that in tracing developed edges at 400 and 700 nm, a low color ratio will indicate a large component of physical development. No such tendency was observed; in all cases the color ratio across the edge remained unity or rose above 1, indicating that physical development does not play an important part in edge enhancement.

#### EFFECT OF SLIT WIDTH ON EDGE STRUCTURE

Figure 8a shows a microdensitometer trace of the object razor blade slit itself, taken with a ratio arm of 100:1 and a scanning slit width of  $10\mu$  (equivalent). This trace shows no edge effect whatever, indicating that the instrument introduces no such effects.

Superposed on Figure 8 are two traces of an edge image processed in XDR-4; both were run with a ratio arm of 100:1, but in one case (8b) the slit width was  $10\mu$  and in the other (8c) the slit width was  $2.5\mu$ . The adjacency peak is pronounced and virtually the same in both cases. We conclude from Figure 8 that since the adjacency edge is not an artifact of the object or of the slit width of the microdensitometer, it is a developer effect that could be further studied.

### FINAL RESULTS

The final results of this program were shown in Figures 1 through 3, and described in the Summary. We explained how the exposures were made and developed; each was traced separately in blue and in red light, using appropriate filters in both

c. Plus-X XDR-4 Slit =  $2.5\,\mu$  b. Plus-X XDR-4 Slit =  $10\,\mu$  a. Trace of Razor Edge

Figure 8. Slit Effects

sample and balancing beams. Microdensitometer conditions were as follows:

Microscope objective - 20X (40X equivalent)

Scanning slit  $-10\mu$  equivalent

Ratio arm -500:1

Filters — Ilford-301 (blue-400), Ilford-204 (red-700)

Balancing wedge - D-355, 0.071 density units/cm displacement.

For images processed in D-19 (Figure 1), we observe a  $\Delta D$  for both blue and red traces of 7.8  $\pm$  0.2 cm, or  $\Delta D$  = 0.55. The blue and red traces are identical until  $D_{max}$  is reached, at which point D(400) rises above D(700) by about 1/78. This is virtually a color ratio of unity. No marked border or fringe adjacency effect is apparent.

In Figure 2 we consider the traces of the XDR-4 developed images;  $\Delta D$  is approximately  $6.6 \pm 0.2$  cm for a  $\Delta D$  of about 0.47. In this figure the blue and red curves are displaced by about 1 mm ( $2\mu$  at 500:1 ratio on the image). This results from imperfect realignment of the traces when they are successively scanned after changing filters. Subtraction of these two curves would produce an inflection point that is not meaningful, since any two identical traces that are out of alignment will show this effect. A careful consideration of Figure 2 shows that the silver is virtually neutral over the entire density range using XDR-4.

The most striking effect is obtained in Figure 3 on the image processed in BN-1A. The separation of  $D_{max}^{-}D_{min}^{-}$  is about 6.8 cm (red) and 7.2 cm (blue), giving  $\Delta D$  values of about 0.40 (red) and 0.51 (blue). This is a measurable color ratio of about 0.51/0.40 = 1.25. The adjacency or border peak is significant, amounting to about 3.5 cm = 0.25 density units for both blue and red. There is an indication of a fringe dip on the  $D_{min}^{-}$  side, measurable in part because the fog level in this developer is 0.43 as a result of its solvation effect. As in Figure 2, the curves of Figure 3 show a shift of 1 mm (=  $2\mu$ ) with respect to each other. A careful subtraction of D(400-D(700)) shows that this function rises steadily

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from  $D_{min}$  to  $D_{max}$ ; there are no unusual effects near either the fringe or border adjacency peaks. We conclude that the silver becomes warmer as it goes from  $D_{min}$  to  $D_{max}$  and that there are no unusual effects associated with the adjacency region.

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